($MgSO_4$) and reduced to yield 0.3041 g (0.001 33 mol, 99%) of **20b** as a white solid, which is 92.26% deuteriated: mass spectrum (FI, M^+ (relative intensity)) *m/e* 232 (1331), 231 (15 207), 230 (144 498), 229 (52 503), 228 (151 675), 227 (37 736), 226 (830). The same procedure was used for deuteriation of the other amides.

Reactions of Amides with *n*-Butyllithium. To a solution of amide **20** dissolved in 20 mL of dry THF at −78 °C under N_2 was added the butyllithium via a syringe pump at the rate of approximately 1 mL/min. The reaction was stirred for 30 min and then quenched with 0.5 mL of MeOH. The solution was washed with water and extracted with ether. The ether extracts were combined, washed with brine, dried over $MgSO_4$, and reduced in vacuo to yield a mixture of **20** and **24**, which was analyzed by GC, separated, and purified if necessary. "Slow stirring" reactions are conducted with the agitation of a magnetic stir bar. "Fast stirring" reactions are conducted with an overhead mechanical stirrer.

Reaction of 2-Bromo-*N*-ethylbenzamide-*N*-*d* (20a d). To 0.1201 g (0.525 mmol) of amide **20a** d dissolved in 20 mL of dry THF at −78 °C under N_2 was added 0.42 mL of 1.26 M *n*-BuLi (0.525 mmol). The reaction mixture was stirred for 30 min and quenched with 0.5 mL of MeOH. Solution was washed with water and extracted with ether. Ether extracts were combined, washed with brine, dried over $MgSO_4$, and reduced in vacuo to yield an off-white solid mixture of 58% of **20a** and 42% of **24a** according to GC. The mixture was separated by MPLC with 30% EtOAc/hexane as eluent to yield 0.0609 g (0.267 mmol, 51%) of **20a** and a 0.0344 g (0.231 mmol, 44%) of **24a**. The mass spectrum showed **24a** to 94.11% deuteriated. Data from **20a**: ^1H NMR (200 MHz) δ 7.20–7.67 (m, 4 H, Ar H), 5.94 (br s, 1 H, NH), 3.48 (dq, 2 H, CH_2), 1.28 (t, 3 H, CH_3); GC (155 °C isothermal) t_R 2.63 min; mp 92–94 °C. Data from **24a**: ^1H NMR (200 MHz) δ 7.30–7.71 (m, 4 H, Ar H), 6.11 (br s, 1 H, NH), 3.50 (dq, 2 H, CH_2), 1.26 (t, 3 H, CH_3); ^{13}C NMR (300 MHz) δ 21.41, 45.26, 125.83, 126.10, 126.23, 130.66, 131.30, 139.46, 173.60; mass spectrum, (FI, M^+ (relative intensity)) *m/e* 147 (525), 148 (7060), 149 (42 486), 150 (464 758), 151 (54 158), 152 (4175).

Fast stirring: 0.1183 g (0.517 mmol) of amide was treated with 0.40 mL of 1.26 M *n*-BuLi (0.504 mmol) to yield 66% **20a** and 34% **24a**.

No stirring: 0.134 g (0.134 g (0.586 mmol) of amide was treated with 0.44 mL of 1.34 M *n*-BuLi (0.590 mmol) to yield 56% **20a** and 44% **24a**.

Acknowledgment. We are grateful to the National Institutes of Health and to the National Science Foundation for support of this work.

Supplementary Material Available: Experimental data for **20b–f** and the reaction of amides **1a–f** with *n*-BuLi (2 pages). Ordering information is given on any current masthead page.

Heterogeneous Catalytic Hydrogenation of Poly(vinylethylene)

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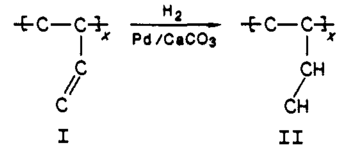
Received October 14, 1987

Abstract: The hydrogenation of poly(vinylethylene) in cyclohexane (1% w/v) at 70 °C with use of a calcium carbonate supported palladium catalyst has been investigated. Evaluation of partially hydrogenated polymer by size-exclusion chromatography and ^1H NMR spectroscopy reveals that this reaction initially proceeds by the concerted hydrogenation of approximately 85% of the unsaturated repeat units in individual polymer molecules during a single adsorption step from solution. This finding is qualitatively explained on the basis of the unique adsorption characteristics of polymers, in conjunction with the estimated heats of adsorption for unsaturated and saturated hydrocarbons on group VIII metal surfaces.

In recent years fully saturated hydrocarbon polymers have been recognized as outstanding materials for studying the fundamental physical properties of polymers in general. Perhaps the most successful route to obtaining monodisperse model polyolefins, which cannot be directly polymerized by any known method, is the hydrogenation of anionically polymerized dienes. This process imparts excellent oxygen, radiation, and thermal stability to unsaturated hydrocarbon polymers. Butadiene,[1-3] isoprene,[3,4] and 2-methyl-1,3-pentadiene[5] have been anionically polymerized by various researchers into a variety of microstructures, which have been shown to be easily transformable to the fully saturated form by hydrogenation in cyclohexane at approximately 70 °C, with use of a palladium catalyst supported on calcium carbonate.

We have recently implemented this hydrogenation method in our laboratory in order to prepare model saturated polymers for the investigation of isotope effects.[6] We discovered that this heterogeneous catalytic hydrogenation reaction proceeds by a mechanism that appears to be unique to polymers and describe here our initial findings concerning this mechanism, which is qualitatively shown to result from the general behavior of polymer solutions in contact with solid surfaces. We make use of the following model reaction in cyclohexane for this purpose:



I II

where I and II are referred to as poly(vinylethylene) (PVE) and poly(ethylethylene) (PEE), respectively, and *x* = 3070.

Experimental Section

Monodisperse poly(vinylethylene) was synthesized by using the anionic polymerization technique. Butadiene monomer (Matheson, instrument purity) was purified by successive distillation from dibutylmagnesium and *n*-butyllithium. Benzene (Aldrich) was distilled from polystyryllithium under purified argon just prior to use as the polymerization medium. The polymerization was initiated with *n*-butyllithium (Aldrich, 1.5 M) in the presence of 1,2-dipiperidinoethane (DPE) (Aldrich) at 6 °C; the ratio of DPE to lithium was 3. Polymerization of butadiene under these conditions has been shown to result in >99% 1,2 addition.[2] The reaction was terminated with degassed methanol, and the product was dried under vacuum and stored in a dark, purified argon environment.

Hydrogenation reactions were carried out in a 2-L Parr reactor at ca. 500 psi of hydrogen and at 70 °C. In all cases the concentration of PVE was 10 g/L of cyclohexane solution; the cyclohexane was distilled from potassium/benzophenone and stored under purified argon prior to use. A palladium catalyst dispersed on calcium carbonate (Strem Chemical Inc.; 5% by weight Pd; 5–10 m^2 g^{-1} active surface area) was employed at concentrations of 0.5, 1, and 1.8 g/g of polymer; these reactions will be referred to as A, B, and C, respectively. Reaction A was sampled 16

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Table I. Hydrogenation Reaction Conditions[a]

reaction	wt of catalyst[b]/ wt of polymer	time, h	conversion,[c] %
A1	0.5[d]	0.04	7
A2	0.5[d]	0.10	10
A3	0.5[d]	0.15	13
A4	0.5[d]	0.20	16
A5	0.5[d]	0.27	20
A6	0.5[d]	0.33	25
A7	0.5[d]	0.40	27
A8	0.5[d]	0.48	30
A9	0.5[d]	0.65	35
A10	0.5[d]	0.92	41
A11	0.5[d]	1.43	49
A12	0.5[d]	2.43	56
A13	0.5[d]	4.38	64
A14	0.5[d]	7.42	67
A15	0.5[d]	21.92	78
A16	0.5[d]	49.58	81
B	1.0[e]	7	47
C	1.8[d]	24	~100

[a] 1% (w/v) polymer in cyclohexane at 70 °C. [b] Strem Chemical Co. $Pd/CaCO_3$ (5%). [c] Determined by solution ^1H NMR spectroscopy. [d] Lot 120338. [e] Lot 120669.

times over a 48-h period. Hydrogenation reactions B and C were terminated after 7 and 24 h, respectively, by cessation of stirring, which resulted in sedimentation of the catalyst. In all cases the polymer product was recovered by filtration and precipitation in methanol, followed by vacuum drying and storage under purified argon.

One gram of reaction product B was immersed in 20 mL of 1-octanol (Aldrich) for 11 days at 35.0 °C. The extracted polymer was precipitated in methanol, dried under vacuum, and stored under purified argon. In a separate set of experiments, we determined the θ temperatures for PVE and PEE in 1-octanol to be 39 ± 1 and 33 ± 1 °C, respectively. The efficiency of this extraction method was tested with a PVE–PEE mixture; the liquid extract contained >99.5% PEE as anticipated on the basis of the measured θ temperatures.

The extent of the hydrogenation reactions was determined from ^1H NMR measurements, obtained from 5% (w/v) $CDCl_3$ solutions, with a FX90Q JEOL spectrometer. The weight average degree of polymerization of PEE (reaction product C) was determined to be $N_w = 3070$ (MW = 172 000) on the basis of intrinsic viscosity measurements obtained from THF solutions at 25 °C together with the Mark–Houwink relationship reported by Xu et al.[2] This value also applies to the PVE sample since the hydrogenation technique employed does not induce chain branching, cross-linking, or degradation[2] (see below).

PVE, PEE, and partially hydrogenated PVE samples were examined for molecular weight distribution by size-exclusion chromatography (SEC). Separation of 100 μL of polymer solutions (0.10% w/v) was effected with a pair of Zorbax PSM SEC columns (Du Pont) with THF as the mobile phase at a flow rate of 1 mL/min. Sample elution times were monitored with a differential refractometer. The instrument was calibrated with a series of polystyrene standards (Pressure Chemical Co.). Although the polystyrene-based calibration curve does not provide for the absolute determination of molecular weight for PVE or PEE, it can be used to estimate the polydispersity indices of these samples with fair accuracy.[7] Both PVE and PEE (reaction product C) are characterized by the same monodisperse value, $MW/M_n \cong 1.03$, confirming the absence of side reactions during hydrogenation.

Finally, we characterized the catalyst with transmission electron microscopy (TEM). Catalyst particles were dispersed on a thin carbon film, which was supported by a copper microscope grid, and examined using a JEOL 100CX instrument operated at 100 keV.

Results and Analysis

The results of the ^1H NMR and SEC measurements are listed in Table I and illustrated in Figures 1 and 2. First we evaluate the product of reaction C. As indicated by ^1H NMR analysis (Table I), reaction C proceeded to completion, yielding a fully saturated product. With the exception of elution time, the SEC traces of the precursor PVE and the PEE product (see Figure 1) are indistinguishable, verifying the absence of side reactions during hydrogenation. Owing to a significantly smaller statistical segment length (a),[2,6] the PEE molecules (a = 5.0 Å) are characterized by a smaller hydrodynamic volume in dilute solution than are the PVE molecules (a = 6.0 Å). As a consequence, the saturated polymer exhibits a longer SEC retention time than the unsaturated polymer, as shown in Figure 1a,b. Because these polyemrs are nearly monodisperse, this difference in retention time is sufficient to separate a PVE–PEE mixture. We have illustrated this point in Figure 1c for a mixture containing 47% PEE.

Next, we analyze the product of reaction B. On the basis of the ^1H NMR results, this reaction proceeded to 47% of completion (Table I). However, this extent of reaction does not reflect a

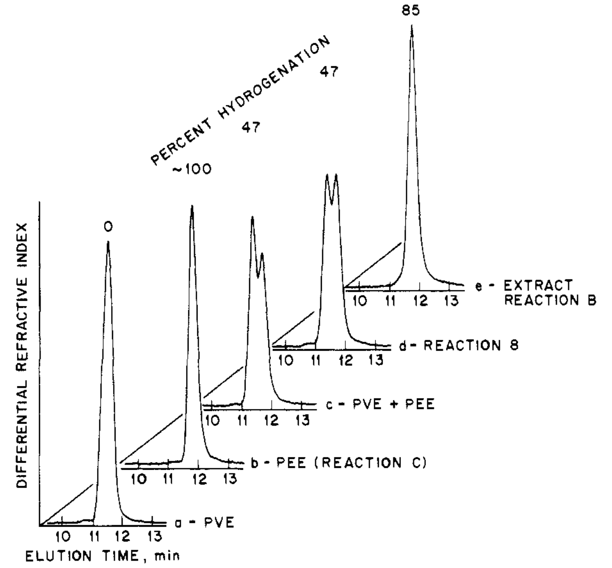

Figure 1. Size-exclusion chromatographs of (a) poly(vinylethylene), (b) poly(ethylethylene) obtained by the complete hydrogenation of poly(vinylethylene), (c) a poly(vinylethylene) (53%)–poly(ethylethylene) (47%) mixture, (b) product of reaction B, (e) polymer extracted from the product of reaction B with a solvent and temperature selective for poly(ethylethylene). The indicated percent hydrogenation was determined by solution ^1H NMR spectroscopy.

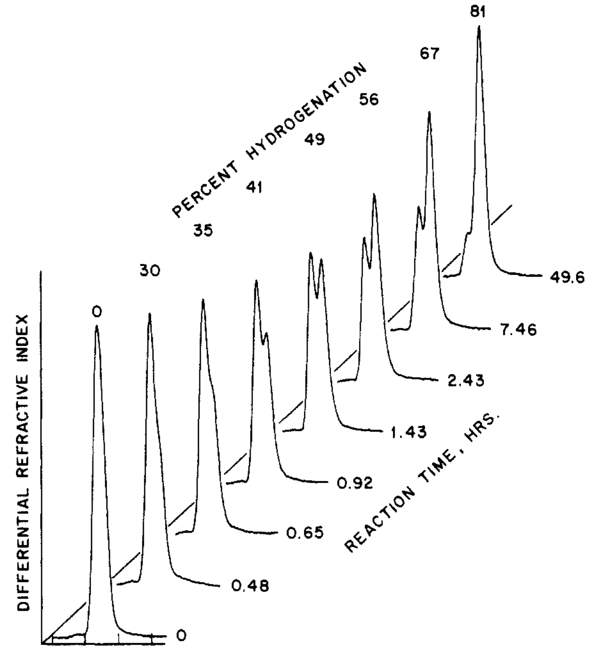

Figure 2. Size-exclusion chromatographs obtained from samples taken during reaction A, demonstrating the binary distribution of polymer species that evolves during the hydrogenation of poly(vinylethylene) to poly(ethylethylene). The peak appearing at longer retention times derives from approximately 85% hydrogenated polymer.

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(7) Because dilute solutions of PVE, PEE, and polystyrene in THF are characterized by similar molecular weight exponents in the respective Mark–Houwink relationships, the SEC calibration curve for the latter can be used to obtain a reasonable estimate of polydispersity for PVE and PEE.

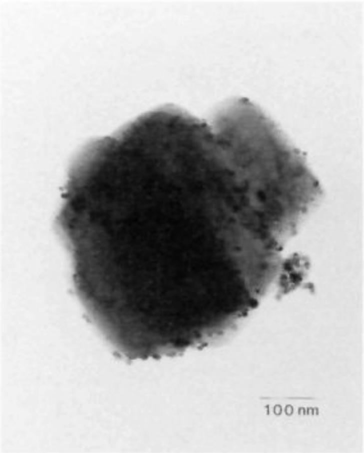

Figure 3. Transmission electron micrograph of a Pd/CaCO$_3$ catalyst particle. The small, dark features correspond to 25–100 Å diameter palladium crystallites that are dispersed on a larger calcium carbonate support particle.

random hydrogenation of 47% of all available vinyl repeat units. As shown in Figure 1d, reaction B produced a bimodal distribution of SEC retention times, which closely resembles the chromatograph obtained from the PVE–PEE mixture (Figure 1c). Polymer extracted from product B using 1-octanol at 35.0 °C produces a monodisperse SEC trace (Figure 1e), which is nearly coincident with that for PEE (Figure 1b). ^{1}H NMR analysis of the separated polymer revealed that 85% of the repeat units are saturated, consistent with the extraction conditions, which strongly favor dissolution of PEE rich polymer (see the Experimental Section). The presence of 15% residual vinyl repeat units in the extracted component accounts for the minor difference in shape between the SEC traces from sample B (Figure 1a) and the PVE–PEE mixture (Figure 1c). We conclude that reaction B resulted in a bimodal distribution of polymers consisting of unreacted PVE and 85% (on average) hydrogenated PVE.

Finally, we consider reaction A, which was sampled continuously during hydrogenation over a 2-day period. In Figure 2 are presented representative SEC traces, which graphically illustrate the course taken by the reaction. This series of chromatographs clearly indicates that the reaction proceeded predominantly by the concerted hydrogenation of PVE molecules to relatively high conversion. The SEC result at 49% conversion is nearly identical with that obtained from reaction B (47% conversion, Figure 1d), indicating that the peak that evolves at longer SEC retention times in Figure 2 corresponds to partially ($\cong$85%) hydrogenated polymer. In fact, the entire sequence of SEC traces obtained from reaction A can be closely reproduced by a convolution of the SEC results given in Figure 1a,e, on the basis of a total degree of saturation dictated by the ^{1}H NMR results (Table I).

TEM analysis of the Pd/CaCO$_3$ catalyst revealed a distribution of approximately 25–100 Å diameter palladium crystallites on the surface of the CaCO$_3$ support. An electron micrograph of a small catalyst particle is shown in Figure 3; average-size catalyst particles are not sufficiently transparent to electrons to allow resolution of the Pd crystallites. On the basis of the reported palladium content (5% w/w) and surface area (5–10 m^2/g^{-1}), we calculate an average particle dimension (d) of 21–42 Å, assuming cubic (volume = d^3) palladium crystallites. This is in excellent agreement with the TEM results.

Before discussing the bimodal distribution of the polymer species that evolves during the hydrogenation of poly(vinylethylene), we comment briefly on the general features of this heterogeneous catalytic reaction.

In order to ensure complete hydrogenation in approximately 24 h we have found that catalyst loadings of between 1 and 2 times the weight of polymer are required, as evidenced by the results obtained from reactions A and C (see Table I); note that the absolute catalyst activity varies between catalyst lots, e.g., compare reactions A14 and B in Table I. Presumably the lack of complete reaction for lower catalyst concentrations reflects catalyst poisoning from unidentified impurities. For reaction C, which went to completion, an average palladium crystallite (d = 21–42 Å) hydrogenated 5–36 polymer molecules, corresponding to a total of (0.2–1.1) × 10^5 vinyl groups.

The most striking feature of these catalytic reactions is the distribution of hydrogenated repeat units at early and intermediate conversions (0–85%). Our SEC results for reaction A (Figure 2) clearly show that for up to 81% overall conversion poly(vinylethylene) molecules are hydrogenated in a concerted fashion. Both the products of reaction A and the extracted (hydrogenated) component of reaction B (Figure 1) indicate that this process involves the hydrogenation of approximately 85% of the repeat units of individual polymer molecules, *which must occur during single adsorption steps*. We believe this result derives from the unique characteristics exhibited by polymers in contact with surfaces.

Discussion

The past three decades have been marked by a steady improvement in the understanding of polymer–surface interactions, driven in part by a variety of practical applications such as adhesion, colloid stabilization, and medical materials. However, we are unaware of any reports describing the impact of polymer–surface science on heterogeneous catalysis. In order to explain our findings for the hydrogenation of poly(vinylethylene) on dispersed palladium, we briefly discuss three aspects of polymer adsorption on solid surfaces: residence time, equilibrium structure, and conformational dynamics. A comprehensive discussion of the second, and most developed of these topics, has been presented in an excellent review article by Takahashi and Kawaguchi.[8]

For reaction A the degree of hydrogenation is approximately linear in reaction time, up to 25% conversion (see Table I). On the basis of the palladium crystallite size described above, and assuming each crystallite can accommodate one polymer molecule, which is 85% hydrogenated during an adsorption step, we calculate a polymer residence time of 30–260 s during the early stages of this reaction; this corresponds to a turnover frequency of (2.8–5.6) × 10^{-2} vinyl groups s^{-1} (Pd atom)$^{-1}$. This residence time is smaller by at least 1 order of magnitude than the residence times reported for various adsorbed polymers in contact with dilute or semidilute solutions.[9,10] Therefore, we conclude that polymer desorption is driven primarily by the hydrogenation reaction.

A variety of factors influence the structure of a polymer adsorbed on a solid surface, including degree of polymerization, polymer concentration in solution, and polymer–solvent, polymer–surface, and solvent–surface interaction energies. For the present discussion, we believe the most important factor is the difference in the energies of interaction between solvent molecules and the surface and polymer segments and the surface. This difference is denoted χ_s and is generally expressed in units of kT where k is the Boltzmann constant. Below a critical value $\chi_{sc} \approx {}^1/_3$, adsorption does not occur,[12] while for $\chi \gtrsim 3$ Scheutjens and Fleer[12] calculate that polymer segment surface coverage approaches unity.

In order to estimate the adsorption characteristics of poly(vinylethylene) and poly(ethylethylene) on palladium, we make use of the reported behavior of butene and butane on platinum. To our knowledge this system provides the closest reported monomeric analogue to the polymeric system we have studied; here we note that the heats of adsorption of olefins on platinum and palladium are very similar, as evidenced by the results published for ethylene on these surfaces.[13,14] Salmeron and Somorjai report heats of

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adsorption of 8.2 and 10.5 kcal mol^{-1} for butane[15] and butene,[13] respectively, on Pt(111) on the basis of thermal desorption spectroscopy (TDS) measurements. Presumably the heat of adsorption per carbon atom (e.g., lattice site) for cyclohexane will be close to that of poly(ethylethylene) on the basis of the evidence presented by Salmeron and Somorjai for other saturated alkanes.[15] As a consequence, χ_s for poly(ethylethylene) will be near or less than χ_{sc}, and this polymer will either weakly adsorb or not adsorb on palladium from solution in cyclohexane. Use of the heats of adsorption for butene and butane as representatives of poly(vinylethylene) segments and cyclohexane (per lattice site), respectively, leads to $\chi_s \cong 3.4kT$ at 70 °C. We note that this calculation represents a lower limit for χ_s since the TDS measurements sample the most weakly bound species in a high coverage limit. For example, independent calorimetric measurements at low surface coverages indicate that the heat of adsorption of ethylene on various group VIII elements is approximately 50–70 kcal mol^{-1},[16] in comparison with the TDS determined value of 12 kcal mol^{-1} for platinum and palladium.[13,14] Therefore, poly(vinylethylene) almost certainly adsorbs strongly ($\chi_s \geq 3$) on palladium from solution in cyclohexane, with nearly complete surface coverage by polymer segments.

An estimate of the fraction of polymer chain segments p in contact with a surface at equilibrium can be made with use of the numerical results presented by Scheutjens and Fleer.[12] Although they have not specifically considered the system we have examined, their calculations in the limit of strong adsorption ($\chi_s \geq 3$) and high degree of polyermization are readily extrapolated to our case. For a 1% solution of polymer characterized by $N \cong 3000$ and $\chi_s = 3$, we estimate $p \cong 0.3$ and 0.6 for θ ($\chi = 0.5$) and athermal ($\chi = 0$) solutions, respectively. Since, in general, $0.4 \lesssim \chi \lesssim 0.5$ for hydrocarbon polymers in hydrocarbon solvents,[17] poly(vinylethylene) in cyclohexane is most likely best represented by the θ solvent estimate ($p \cong 0.3$). In addition, the restricted surface area afforded by the finite size of the palladium crystallites will diminish the actual value of p to some extent. From these arguments we conclude that the observed 85% polymer chain hydrogenation must involve significant rearrangement of the (partiallly hydrogenated) polymer molecules on the palladium surface.

Our picture of the early stages of poly(vinylethylene) hydrogenation is as follows. Initially the unsaturated polymer molecules are strongly driven to adsorb on palladium crystallites due to a highly favorable ($\chi_s \lesssim 3$) interaction energy between the olefinic repeat units and the metal surface. Subsequent hydrogenation reduces the affinity of the polymer toward the surface. However, the molecule is sufficiently dynamic to allow for significant conformational rearrangement, thereby presenting unreacted unsaturated repeat units to the surface, which both prolongs adsorption and leads to an increase in the degree of hydrogenation over that expected from the estimated equilibrium fraction ($p \cong 0.3$) of adsorbed polymer segments. On average, the molecule desorbs after hydrogenation of approximately 85% of the repeat units. Experiments demonstrate that with sufficient catalyst concentrations subsequent adsorption steps lead to complete hydrogenation.

Finally, we speculate on what influences the degree of conversion during the first adsorption step. Clearly, in the limit of an extremely long residence time (as is generally observed for polymers[9,10] and a relatively rapid rate of conformational rearrangement (relative to polymer adsorption times), all unsaturated repeat units would have access to the surface and ultimately be hydrogenated. At least two factors can be identified that operate against complete conversion during the first adsorption step. First, unhydrogenated poly(vinylethylene) in solution competes for the metal surface with the partially hydrogenated adsorbed polymer. With increasing saturation, the residence time will decrease since the driving force for displacement by poly(vinylethylene) molecules increases (in fact, if $\chi_s < \chi_{sc}$ for poly(ethylethylene) the residence time may become zero prior to complete saturation even in the absence of poly(vinylethylene) molecules). If this represents the limiting factor in determining the degree of hydrogenation at desorption, we expect the polymer concentration to influence this parameter. Second, in the event of rapid polymer segment hydrogenation kinetics, the dynamics of conformational rearrangement may be too slow to accommodate the surface with unreacted vinyl groups, presumably present in the form of loops and tails.[18] Desorption would then result due to an effectively (locally) diminished χ_s. In this case, the degree of hydrogenation at desorption should depend strongly on molecular weight.

We close by suggesting several experiments that could shed considerable light on the questions posed by our results. Evaluation of the distribution of reacted and unreacted repeat units in the once adsorbed polymer by high-resolution NMR spectroscopy (e.g., random versus block distribution) would provide valuable information with which to discriminate between various models for the behavior of these polymers on catalytic surfaces. Varying the polymer molecular weight and molecular weight distribution (e.g., tailoring the distribution by mixing monodisperse polymers) would directly test the aforementioned theories for polymer adsorption. For example, the distribution of polymer species generated during the hydrogenation of a binary mixture of monodisperse poly(vinylethylene) could be followed directly by SEC; for a sufficient difference in the molecular weight of the two starting polymers, four SEC peaks should be resolvable at early and intermediate conversions. Conducting hydrogenation reactions in different solvents should alter χ_s and consequently lead to a change in the extent of hydrogenation during the first adsorption step. Further, the hydrogenation of block copolymers containing two different unsaturated repeat units, or blocks of unsaturated repeat units separated by unreactive spacer blocks, may provide insight into the thermodynamics and dynamics of these reactions. Obviously, elucidation of the detailed mechanisms that dictate the heterogenous catalytic hydrogenation of unsaturated hydrocarbon polymers will require a significant amount of additional research. We believe these initial findings should provide guidance in developing a more complete understanding of this interesting class of reactions.

Summary

We have examined the process of hydrogenating poly(vinylethylene) dissolved in cyclohexane (1% w/v) with use of a calcium carbonate supported palladium catalyst at 70 °C. On the basis of size-exclusion chromatography and ^{1}H NMR analyses, we conclude that this heterogeneous catalytic reaction initially proceeds by the concerted hydrogenation of approximately 85% of the unsaturated repeat units of individual poly(vinylethylene) molecules, during a single adsorption step. This finding can be qualitatively explained by using the absorption energies reported for saturated and unsaturated simple hydrocarbon molecules on group VIIIA metals, in conjunction with current theories describing the adsorption characteristics of polymers from solution.

Acknowledgment. We are grateful to H.D. Keith for his assistance in obtaining the TEM pictures, to M. Tirrell, R. Nuzzo, L. Dubois, B. Bent, and T. M. Duncan for valuable discussions and suggestions, and to E. A. Chandross for a helpful critique of the manuscript.

Registry No. Pd, 7440-05-3; polybutadiene, 9003-17-2.

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